

Voltammetric Study of the Electrocatalytic Activity of the Copper Alloys for the Nitrate Reduction in Weakly Alkaline Solution

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Ion exchange represents a well established method for the removal of nitrates from drinking and technological water. During regeneration of saturated ion exchanger large volumes of solution containing relatively high nitrate concentration are produced. Previous study on the electrocatalytic activity of different electrode materials for nitrate reduction in weakly alkaline solutions used for the regeneration of strongly basic ion exchanger revealed copper to be most electrocatalytically active among the tested materials (1). Its polarization curve exhibited after subtraction of the blank experiment two overlapping cathodic current peaks corresponding to the nitrate reduction reaction. Using the rotating ring-disk electrode (RRDE) first peak was identified to correspond to reduction of nitrate to nitrite. Using batch electrolysis ammonium was identified as the main reduction product. It is produced in the region of the second, more cathodically located peak. Even we are dealing with the regeneration solution and thus drinking water is not contaminated, it is an undesirable product. Alloys of copper were tested in the present study using cyclic voltammetry on the RRDE. The aim was to determine influence of the presence of an additional metal in the cathode structure on its electrocatalytic activity and selectivity.

Tin bronze and brass were studied in the first step. The brass electrode exhibits in comparison to the copper electrode a pronounced shift of the current peak to the more cathodic potentials. Using the brass disk electrode platinum ring electrode shows high anodic current response. It indicates that product of the nitrate reduction is oxidisable in the whole potential range of nitrate reduction. This is in contrast to copper cathode as discussed below. Moreover, using brass cathode current response was observed on the ring electrode polarised more anodically than 0.70 V vs. SCE. Using copper cathode current response was observed on the ring electrode polarised more than by 0.95 V vs. SCE. It indicates different reduction products are formed at these two materials. Since the product is reactive nitrogen compound, brass was not further supposed as an appropriate material for this process.

Bronze shows more promising properties. The potential range of the nitrate reduction is similar to copper (see Figure). The number of observed cathodic current peaks, however, is for bronze higher. This is because of the more pronounced potential separation of individual reduction mechanism steps. Reaction mechanism similar to copper electrode at least in the first reduction steps is indicated by almost identical current response on the ring electrode. It shows nitrite oxidation peak in the potential region of the first peak on the disk electrode. As mentioned above it corresponds to the first nitrate reduction mechanism step. The relation of the peak current densities is different for the both cathode materials. It indicates kinetics of individual mechanism steps to be influenced on diverse way by the electrode

material composition. This difference is further pronounced by variation of the electrode rotation and potential sweep rates variation. It may provide possibility to control final reaction product by the cathode potential (or directly related current density) and thus avoid formation of undesired species.

From the experimental results it is possible to conclude that alloying of copper with another metal(s) provides an attractive way to influence its electrocatalytic selectivity and thus minimize formation of undesirable compounds as a nitrate reduction final product. Wider spectrum of the materials as well as more detail analysis of the reduction mechanism has to be provided in order to establish dependence between the cathode composition and electrocatalytic selectivity.

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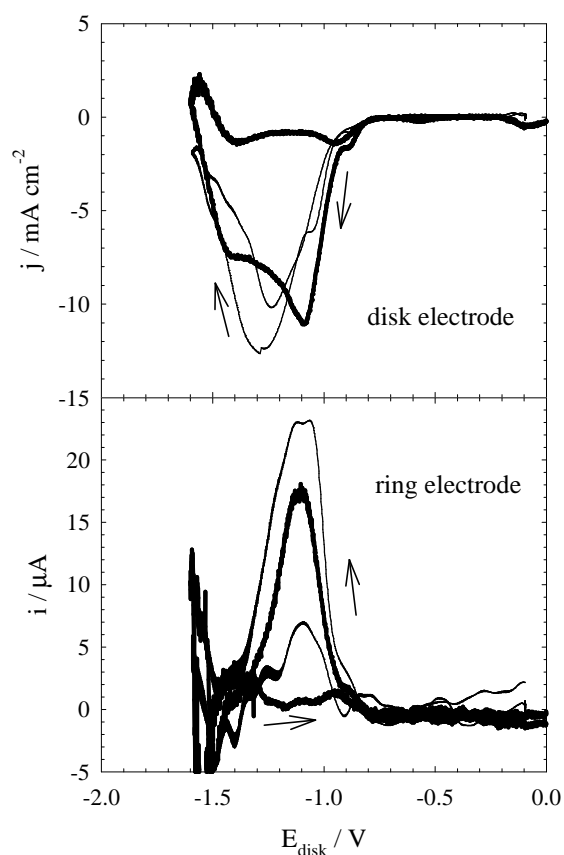


Figure: Cyclic voltammetric curve on RDE electrode and Pt ring electrode in the electrolyte containing NO_3^- ions after subtraction of the blank experiment, potential scan rate 10 mV s^{-1} , potential of ring electrode 1.0 V. Thin line – copper electrode, bold line – bronze electrode. Potentials refer to the SCE.